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Field assessment of treatment efficacy by three methods of phosphoric acid application in lead-contaminated urban soil

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Abstract

In situ soil treatment using phosphoric acid (H_3PO_4) may be an effective remedial technology for immobilizing soil Pb and reducing Pb risk to human health and ecosystem. The treatment efficacy of three H_3PO_4 application methods was assessed in a smelter-contaminated urban soil located in the Jasper County Superfund Site, Missouri. Soil, with an average of 3529 mg Pb kg^{-1} and in the 2- by 4-m plot size, was treated with H_3PO_4 at a rate of 10 g P kg^{-1} in four replicates by each of three methods: rototilling; surface application; pressure injection. Three soil cores, 2.5-cm diameter and 30-cm long, were taken from each plot before and 90 days after treatment and analyzed for soluble P, bioaccessible Pb and solid-Pb speciation. Applications of H_3PO_4 induced the heterogeneity of soluble P in soil, with the highest concentrations in the surface. Three application methods mixed the H_3PO_4 more effectively in the horizontals than the verticals of treated soil zone. The H_3PO_4 applications significantly reduced Pb bioaccessibility in the soil, which was influenced by the concentrations of soil soluble P and solid-Pb species. The risk reductions of soil Pb were achieved by formation of pyromorphites or pyromorphite-like minerals. The rototilling appears to be the most effective treatment method in context of the homogeneity of soluble P and the reduction of Pb bioaccessibility in treated soil.
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1. Introduction

Elevated lead (Pb) in soil has been identified as a threat to human health and ecosystem (Cotter-Howells and Thorton, 1991; US Environmental Protection Agency, 1998). The risk of soil Pb to human health depends on the ability of oral-ingested Pb that dissolves in the gastrointestinal tract and elevates blood-Pb level (Ruby et al., 1996; Casteel et al., 1997), and the ecological threat is associated with Pb mobility in soil system (Bubb and Lester, 1991), which both are controlled by the chemical or mineralogical associations of soil Pb and their solubility (Ruby et al., 1992; Davis et al., 1993). Immobilization or transformation of soil Pb to low soluble species that reduces Pb dissolution in the gastrointestinal tract and leachability in soil system may be a remedial strategy for Pb-contaminated soil, which safeguards human and ecosystem from the contamination.

Immobilization of soil Pb can be achieved by formation of pyromorphite through phosphate amendments.

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Pyromorphite is an insoluble lead phosphate [$Pb_5(PO_4)_3$ (OH, Cl, F. . .)] and chemically and biologically stable under the surface soil conditions. Application of phosphate-based amendments, including synthetic hydroxyapatite, phosphate rocks, triple superphosphates, has been shown to effectively remove Pb from aqueous and soil solution (Ma et al., 1993, 1995; Xu and Schwartz, 1994; Laperche et al., 1996; Zhang et al., 1998), to reduce Pb bioavailability and phytoavailability in soil (Ruby et al., 1994; Laperche et al., 1997; Hettiarachchi et al., 2000), and to minimize leachable Pb in industrial wastes (Eighmy et al., 1997, 1998; Crannell et al., 2000).

Formation of pyromorphite is kinetically rapid chemical processes that involve dissolution of Pb solids, followed by precipitation of soluble Pb with soluble P. The reaction rate is controlled by the dissolution rate of the Pb-solids and availability of soluble P. Lowering soil pH was found to significantly enhance dissolution of soil Pb and favor the reaction toward pyromorphite formation (Zhang et al., 1998). Application of phosphoric acid (H_3PO_4) that would lower soil pH and provide highly soluble P is believed to be a most effective remedial treatment in calcareous soil for maximum reduction of Pb exposure to human and ecosystem. Treatment using H_3PO_4 to smelter or battery contaminated soils has demonstrated to effectively reduce soil Pb bioavailability as determined by the in vivo swine test (Casteel et al., 1997) and the in vitro extraction test (Yang et al., 2001), and the Pb leachability as measured by the Toxicity Characteristic Leaching Procedures (Cao et al., 2001) and a simulated column leaching test (Yang et al., 2002).

Although the substantial risk reduction of soil Pb has been achieved by the H_3PO_4 treatment, application methods that treat the soil most effectively under field conditions are largely unknown and little assessed. A field experiment was conducted to evaluate the treatment efficacy of three H_3PO_4 application methods: rototilling; surface application; and pressure injection, in a smelter-contaminated urban soil. Objective of this study is to determine the most effective application method under field conditions by examining the soluble P homogeneity and reduction of Pb bioaccessibility in treated soil zone.

2. Materials and methods

2.1. Site description

The field site selected for the H_3PO_4 treatment was located in Joplin City within the Jasper County Superfund Site, Missouri. The site, 61×46 m in area, was a vacant residential lot and had been Pb-contaminated by a former smelter located about 0.4 km northeast of the site. Preliminary site survey (3.5- by 3.5-m sampling scale) conducted with the X-ray fluorescence spectrometry (XRF) revealed that the Pb concentration in top 15-cm soil varied from 400 to 6000 mg kg^{-1}, with an average of 2200 mg kg^{-1} (Mosby, 1996). The Pb concentrations in soil generally decreased with the distance away from the smelter. The site soil lacked structure, contained 15–20% of rocks and gravels, and had about 30-cm depth.

2.2. Experimental procedures

The experiment consisted of 2- by 4-m plots in randomized complete block design with four replicates of each of three application method plus control. Each plot was bounded by a 25-cm tall plastic edging to prevent the plots from crossing-contamination. Phosphoric acid (fertilizer grade, 85% P_2O_5) was applied to the plots at a rate of 10 g P kg^{-1} by three methods: rototilling; surface application; and pressure injection. Potassium chloride (KCl) was also added to the treated plots at a rate of 500 mg Cl kg^{-1} to provide Cl source for chloropyromorphite formation. The rate of H_3PO_4 or KCl applied was determined based on the batch treatments using similar soil by Yang et al. (2001), and the amounts were calculated for treating the top 15-cm soil.

The top 15-cm soil of the rototill-treated plots was rototilled prior to H_3PO_4 application. Half the amount of H_3PO_4 and KCl were then uniformly applied to each plot and rototilled into the soil, followed by adding the remaining half H_3PO_4 and KCl, and further rototilling. The surface soil of the surface-treated plots were scratched with a garden aerator before treatment, followed by applying half the amount of H_3PO_4 and KCl, and further surface aerating. The procedures were repeated for the remaining half H_3PO_4 and KCl. A minimum of three passes with rototiller or aerator was made for each half amount of H_3PO_4 and KCl without forming significant clods. The soil of the pressure-injected plots were initially amended with KCl, and H_3PO_4 was then injected by a pressure injector into the top 15-cm soil at a distance of 15-cm intervals, with an equal amount of H_3PO_4 for each injection. Predetermined amounts of hydrated lime [$Ca(OH)_2$] were applied to the treated plots 10 days after treatment to raise soil pH up to 6.5–7.0. Seeds of Kentucky tall fescue were planted 30 days after treatment to re-establish the vegetation of the plots.

Table 1
Physiochemical characterization of pretreated soil in the study site

Texture	SIL	Total C	48 g kg^{-1}
Clay	154 g kg^{-1}	Total N	3.4 g kg^{-1}
Silt	578 g kg^{-1}	Avail. P	25.2 mg kg^{-1}
pH	7.1	Solid-Pb species	$PbCO_3$, PbO, $PbSO_4$, PbS
CEC	21.5 meq/100g	Minerals	Quartz, dolomite, feldspar
NA	4.0 meq/100g		Illite, kaolinite

Three soil cores, 2.5-cm diameter and 30-cm long, were taken from each of treated plots at a distance of 1-m intervals before and 90 days after treatment, and cut into 0–5, 5–10, 10–20, and 20–30 cm increments. Twelve samples per plot and 48 samples per treatment were collected. The soils were air-dried, passed a 0.25-mm sieve, and stored at room temperature for the soluble P, bioaccessible Pb, and solid-Pb speciation analyses.

2.3. Analytical procedures

The soils collected before treatment were characterized for clay, silt, and sand content; pH; cation exchange capacity (CEC); neutralizable acidity (NA); total carbon and nitrogen; available phosphate following standard USDA procedures (Soil Survey Investigation Staff, 1996). Total Pb and P were determined by digesting soil with 3:2 HNO_3:$HClO_4$ (Blanchar et al., 1968), followed by the induced couple plasma atomic emission spectrometry (ICP-AES). Soil mineralogy was characterized by the X-ray diffraction (XRD), and solid-Pb species by the electron beam microprobe (Link et al., 1994).

The soils collected before and after treatment were analyzed for bioaccessible Pb, and the treated soils analyzed for soluble P and solid-Pb species. Lead bioaccessibility is an estimate of Pb bioavailability, which simulates dissolution of soil Pb in the gastrointestinal tract by an in vitro chemical extraction. In this study, bioaccessible Pb was extracted using a 0.011 M HCl (pH 2) solution with a 1:100 soil:solution ratio at 30 rpm at 37 °C for 60 min, and determined by atomic absorption spectrophotometry (AAS) in a 0.1% La solution (Yang et al., 2001). Soluble phosphate in soil was extracted using 0.011 M HCl solution at 1:100 soil:solution ratio for 60 min and measured by colorometry using the molybdenum blue method. Elemental composition of the Pb solids was analyzed by the electron beam microprobe technique using the wavelength dispersive spectroscopy (WDS) as described by Yang et al. (2001).

3. Results and discussions

3.1. Soil characterizations

Characterization of the pretreated soil indicated that the soil was a calcareous silt loam with relatively high carbon and low phosphate (Tables 1 and 2). The mineralogy showed that dolomite and feldspar were major minerals besides quartz in the sand and silt fractions (>2 μm), respectively, and illite and kaolinite in the clay fraction (<2 μm). Presence of dolomite might contribute to high carbon and alkaline conditions of the soil. The soil contained an average of 3529 mg Pb kg^{-1} with major solid-Pb species of cerrusite ($PbCO_3$) and lead oxides (PbO), and minor anglesite ($PbSO_4$) and galena (PbS). Relatively high total Pb and low P concentrations, labile Pb-bearing solids ($PbCO_3$, PbO), and alkalinity of the soil would make the H_3PO_4 treatment suitable for Pb immobilization.

Measurements of total and bioaccessible Pb presented high variability across plots and depth. The soils had an averaged coefficient of variation (CV, ratio of standard derivation:mean) of 57% in total Pb (Table 2). The variability across plots (horizontals) was higher than that in depth (verticals) (55% vs. 31%). The variation may reflect the impact of the former smelter with distance and the degree of the airborne particle deposition in different time periods. The variability of bioaccessible Pb in the site had a similar trend as the total Pb. The concentration of bioaccessible Pb (mg kg^{-1}) was found to be highly correlated with the total Pb concentration (mg kg^{-1}) as shown in Eq. (1):

$$\begin{aligned} \text{bioaccessible Pb} &= 903 - 0.105(\text{total Pb}) \\ &\quad + 0.000066(\text{total Pb})^2 \\ R^2 &= 0.63 \end{aligned} \tag{1}$$

The soils had an averaged bioaccessible Pb of 1775 mg kg^{-1}, which accounted for 50% of the total Pb, varying from 13% to 81%. High Pb bioaccessibility could be attributed to labile Pb solids of cerrusite and

Table 2
The variability of total Pb and P, bioaccessible Pb, and pH of pretreated soils in the study site

Analyses	μ	Standard deviation (SD)		
		Total	Horizontal	Vertical
pH	7.16	0.35	0.26	0.28
Total P mg kg^{-1}	295.39	121.95	121.63	78.83
Total Pb mg kg^{-1}	3528.78	1999.15	1954.38	1087.47
Bioaccessible Pb mg kg^{-1}	1775.17	1274.76	1088.97	706.19

Table 3
The variability of soluble P and bioaccessible Pb as influenced by the H_3PO_4 application methods

Application method	μ	Standard deviation (SD)		
		Total	Horizontal	Vertical
Soluble P mg kg^{-1}				
Rototilling	5385.95	1218.71	708.59	1280.27
Surface application	7788.49	1881.48	914.31	1775.01
Pressure injection	1816.19	525.03	458.90	391.74
Bioaccessible Pb mg kg^{-1}				
Rototilling	845	195	188	164
Surface application	460	102	96	87
Pressure injection	1061	159	155	137

lead oxides present in the soils, and high variability of bioaccessible Pb fraction in the total may result from compositional variation of soil Pb solids across plots and depth.

3.2. Homogeneity of soluble phosphate

The transformation of soil Pb to pyromorphites depends on the activity of soluble P and Pb as shown in Eq. (2):

$$5Pb^{2+} + 3H_2PO_4^- + Cl^- \Leftrightarrow Pb_5(PO_4)_3Cl_{(s)} + 6H^+ \quad \log K = -25.05. \quad (2)$$

Pb bioaccessibility and leachability have been reported to decrease with increasing soluble P in soil (Yang et al., 2001, 2002). Thus the assessment of soluble P homogeneity in treated soil zone by the H_3PO_4 applications could be used to evaluate the effectiveness of the application methods for mixing the H_3PO_4 with soil or the treatment efficacy. Not surprisingly, the H_3PO_4 application significantly increased soluble P in the 30-cm depth of the soil regardless of the methods. The surface application resulted in the largest increase with an average of 7788 mg P kg^{-1} in the profile, and the pressure injection had the least increase with an average of 1816 mg P kg^{-1} (Table 3). In soil profile, the largest increases were found in the surface for all three methods, with the highest by the surface application, and the concentrations decreased substantially with depth (Fig. 1). Based on the amounts of the H_3PO_4 added, it was estimated that the top 15-cm soil should have an average of 10,000 mg P kg^{-1} if added P is thoroughly mixed with soil. High accumulation of soluble P in the surface layer indicated that neither rototilling nor surface application effectively incorporate added H_3PO_4 into the treated zones or the vertical-mixing by the methods was less effective. It was also speculated that the lime application after the H_3PO_4 treatment would enhance the stabilization of added H_3PO_4 in the surface by the formation of calcium phosphates or apatite, which prevented the H_3PO_4 from leaching into deeper profile. Lower than expected soluble P in the pressure injection plots suggested that the injected P was localized in the injection zone and failed to uniformly distribute to surrounding soil.

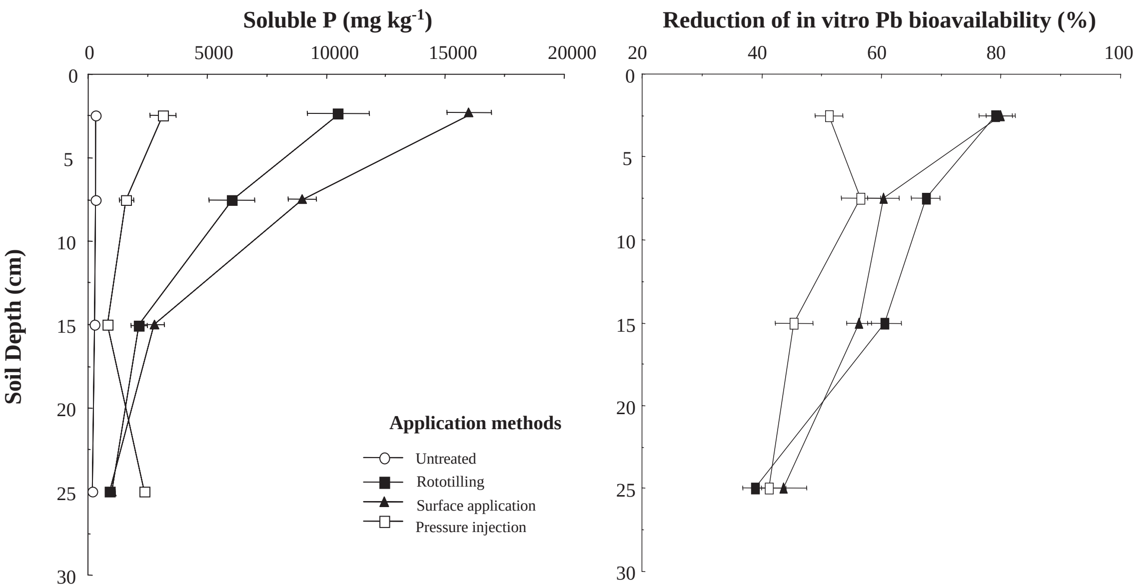

Fig. 1. Depth-distributions of soluble P and reduction of Pb bioaccessibility as influenced by the H_3PO_4 application methods.

In all cases, the H_3PO_4 applications induced a high heterogeneity of soluble P across plots and depths. Averaged CV of soluble P by each of three methods varied from 23% to 29%. The pressure injection caused the highest variability (29% CV) despite of the lowest averaged concentration, while the other two methods had 23–24% CV (Table 3). The rototilling and the surface application were found to have higher variability in the verticals than the horizontals (12–13% vs. 23–24%, respectively), and the pressure injection was the opposite (25% vs. 21%). This implied that both methods mixed the H_3PO_4 more effectively in the horizontals than the verticals. As compared with overall CVs, the rototilling resulted in the lowest variability of soluble P in treated soil, suggesting that the mixing by the rototilling was more homogeneous than that by either surface application or pressure injection. Higher total variability and larger variation of the horizontals than verticals by the pressure injection could reflect the feature of the method in which injected P was heterogeneously distributed in soil. Redistribution of injected P in soil was dependent on diffusion process and largely controlled by H_3PO_4 gradients near injected zone. The diffusive rate was usually very slow and decreased with time. Despite of higher than expected heterogeneity of soil soluble P induced by all three methods, the rototilling demonstrated the most effective for mixing H_3PO_4 in the treated zone in term of the homogeneity of soluble P in soil.

3.3. Reduction of Pb bioaccessibility

Lead bioaccessibility is an estimate of soil Pb that potentially contributes to elevated blood-Pb level or the Pb risk to human health. Thus measurement of Pb bioaccessibility could be used to assess the treatment efficacy for reducing the exposure of soil Pb to human health. Due to a large variation of Pb bioaccessibility present in pretreated plots, the reduction percentage of Pb bioaccessibility by the application methods were assessed by comparing the measurements of individual soil on each plot before and after the H_3PO_4 applications and presented here. Significant reductions of Pb bioaccessibility in the soil were achieved by all three H_3PO_4 applications. An average of the reductions by three application methods was 59%, from 1775 mg kg^{-1} before treatment to 724 mg kg^{-1} after treatment. Data presented in Fig. 1 indicated that the rototilling achieved the largest reduction by 61% across soil depth while the reduction by the pressure injection was 48%. In soil profile, the reductions were highest in the surface and decreased with depth, which was similar to the depth distributions of soluble P in the soil. This suggested that the H_3PO_4 applications had induced the transformation of partial soil Pb to less bioavailable forms and higher concentration of soluble P would enhance the transformation.

Similar to soluble P in soil, Pb bioaccessibility measured after the H_3PO_4 application varied with plot

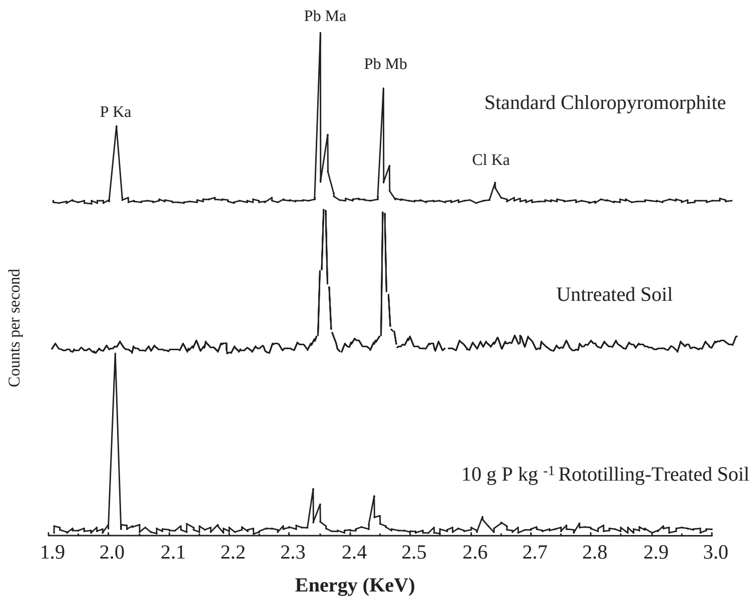

Fig. 2. WDS patterns of analyzed Pb solids in H_3PO_4-treated and untreated soils.

and soil depth. An average of the CV by three application methods was 20%, with the largest CV (23%) by the rototilling and the least (15%) by the pressure injection (Table 3), which was less than that of pretreated plots. Homogenization of the surface soil by the application methods could contribute to overall reduction of the variability of Pb bioaccessibility. However, unlike soluble P, the variations of Pb bioaccessibility were higher in the horizontals than verticals, which was similar to those of total Pb in pretreated soils (Table 2). This implied that the reduction of Pb bioaccessibility by the H_3PO_4 application methods might be influenced by total Pb or Pb species. High total Pb concentration or high fraction of labile Pb species in total is speculated to be more easily transformed to less bioavailable forms by H_3PO_4.

3.4. Solid-Pb speciation

Although measurements of Pb bioaccessibility indicated that a significant portion of soil Pb had been transformed to less bioavailable forms by the H_3PO_4 applications, the measurement did not provide a direct evidence whether pyromorphites are formed after treatment. Thus speciation of the Pb-solids after treatment is important for verifying the immobilization reactions. Selected soil samples were analyzed for elemental composition of Pb-solids by the microprobe technique. The wavelength dispersive spectroscopic (WDS) patterns generating from the Pb-solids in rototilling and pretreated soils were presented in Fig. 2. Microprobe analysis revealed that the Pb solids formed after the H_3PO_4 treatment had a similar WDS pattern to that of synthetic chloropyromorphite standard, indicating that added P and Cl had reacted with soil Pb and been incorporated into the new-formed Pb precipitates. Higher intensity of the P peaks in the Pb precipitates analyzed than the synthetic chloropyromorphite standard might be due to large deposition or super-saturation of the H_3PO_4 around the Pb solids. In pretreated soil, solid-Pb species were primarily cerrusite and lead oxides and showed no P and Cl peaks in the WDS pattern. This analysis had indicated that pyromorphites or pyromorphite-like minerals might be formed after the H_3PO_4 treatment.

This study demonstrates that applications of H_3PO_4 significantly reduce the Pb risk in smelter-contaminated urban soil. The reductions were the highest in the surface and varied with tested application methods. The extent to which Pb bioaccessibility was reduced was influenced by soluble P and solid-Pb species present in soil. Formation of pyromorphite or pyromorphite-like minerals induced by the H_3PO_4 application may be responsible for the reductions of soil Pb risks. Among three H_3PO_4 applications tested, the rototilling is assessed to be the most effective treatment method in terms of the soluble P homogeneity and the reduction of Pb bioaccessibility in treated soil zone.

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